

学校编码: 10384  
学号: 200325034

分类号\_\_\_\_密级\_\_\_\_  
UDC\_\_\_\_

厦 门 大 学  
理 学 硕 士 学 位 论 文

环金属化钯-偶氮配合物作为光学分子传感器的应用初探

**Investigation on the application of Cyclometalated  
Palladium-azo Complexes as Optical Molecular  
Chemosensors**

于春伟

指导教师姓名: 许金钩 教授

李顺华 博士

专 业 名 称 : 分 析 化 学

论文提交日期: 2006 年 5 月

论文答辩时间: 2006 年 7 月

学位授予日期: 2006 年 月

答辩委员会主席:

评 阅 人:

2006 年 7 月

**Investigation on the application of Cyclometalated  
Palladium-azo Complexes as Optical Molecular  
Chemosensors**

A Dissertation Presented

By

**Chun-Wei Yu**

Supervisors:

Professor **Jin-Gou Xu**

Ph.D **Shun-Hua Li**

Submitted to the Graduate School of Xiamen University

for the Degree of

**MASTER OF SCIENCE**

Department of Chemistry, Xiamen University

May, 2006

## 厦门大学学位论文原创性声明

兹呈交的学位论文，是本人在导师指导下独立完成的科研成果。本人在论文写作中参考的其他个人或集体的研究成果，均在文中以明确方式标明。本人依法享有和承担由此论文而产生的权利和责任。

声明人（签名）：

年 月 日

# 厦门大学学位论文著作权使用声明

本人完全了解厦门大学有关保留、使用学位论文的规定。厦门大学有权保留并向国家主管部门或其指定机构送交论文的纸质版和电子版，有权将学位论文用于非赢利目的的少量复制并允许论文进入学校图书馆被查阅，有权将学位论文的内容编入有关数据库进行检索，有权将学位论文的标题和摘要汇编出版。保密的学位论文在解密后适用本规定。

本学位论文属于

1、保密（ ），在 年解密后适用本授权书。

2、不保密（ ）。

（请在以上相应括号内打“√”）

作者签名： 日期： 年 月 日

导师签名： 日期： 年 月 日

## 目录

中文摘要.....	I
英文摘要.....	III
第一章 绪论 .....	1
第一节 光学分子传感器简介 .....	1
1.1.1 光学分子传感器 .....	1
1.1.2 光学分子传感器设计的基本原理 .....	2
1.1.3 过渡金属配合物光学分子传感器 .....	4
第二节 铂族金属配合物光学分子传感器的研究进展 .....	5
1.2.1 铂族钳形配合物光学分子传感器 .....	6
1.2.2 环金属化铂族配合物光学分子传感器.....	10
第三节 论文的设想与目标.....	16
参考文献 .....	16
第二章 四核环金属化钯-偶氮配合物 MOP 作为有机磷农药检测 的分辨型光学分子传感器 .....	24
第一节 引言 .....	24
第二节 分子探针的合成与表征 .....	26
2.2.1 MOP 的合成.....	27
2.2.2 MOP 的表征.....	27
第三节 实验结果与讨论 .....	29
2.3.1 MOP 与有机磷农药的显色反应 .....	29
2.3.2 MOP 与有机磷农药的显色反应的机理探讨 .....	31

2.3.3 溶剂组成对 MOP 与有机磷农药的显色反应的影响 .....	31
2.3.4 MOP 用于有机磷农药定量分析的可行性考察 .....	32
本章小结 .....	35
参考文献 .....	36

### 第三章 双核环金属化钼-偶氮配合物 mop 作为水溶液中硫氰酸根测定的光学分子传感器 .....

#### 39

第一节 引言 .....	39
第二节 分子探针 mop 的合成 .....	40
第三节 实验结果与讨论 .....	41
3.3.1 mop 对硫氰酸根的分辩性光谱识别 .....	41
3.3.2 mop 与硫氰酸根的显色反应的机理探讨 .....	42
3.3.3 mop 与硫氰酸根的显色反应的实验条件优化 .....	44
3.3.4 硫氰酸根定量分析方法的分析性能 .....	45
本章小结 .....	47
参考文献 .....	48

### 第四章 MOP 在其它生理活性物种检测方面应用的初探 .....

#### 51

第一节 MOP 在苯酚、苯胺类化合物识别中的应用初探 .....	51
4.1.1 引言 .....	51
4.1.2 实验结果与讨论 .....	52
4.1.2.1 MOP 与苯酚、苯胺类化合物的显色反应 .....	52
4.1.2.2 MOP 与苯酚、苯胺类化合物的显色反应的机理探讨 .....	54
第二节 MOP 在青霉素 G 及其代谢产物识别中的应用初探 .....	55
4.2.1 引言 .....	55

<b>4.2.2 实验结果与讨论</b>	56
4.2.2.1 MOP对氨苄青霉素在不同代谢条件下的降解过程跟踪	56
4.2.2.2 MOP对不同代谢条件下的青霉素G的光学响应	56
4.2.2.3 实验机理的探讨	57
本章小结	58
参考文献	59
<b>第五章 总结与展望</b>	62
附录 1 仪器与试剂说明	64
附录 2 硕士生阶段发表和交流的论文	65
致谢	66

## Contents

<b>Abstract in Chinese</b> .....	I
<b>Abstract in English</b> .....	III
<b>Chapter 1 Introduction</b> .....	1
<b>1.1 Brief introduction to optical molecular chemosensors(OMCS)</b> ...	1
1.1.1 Molecular chemosensors .....	1
1.1.2 Basic principle of designing optical molecular chemosensors (OMCS) .....	2
1.1.3 Optical molecular chemosensors based on transition metal complexes .....	4
<b>1.2 Research progress on optical molecular chemosensors baesd on         platinum group metal complexes</b> .....	5
1.2.1 Optical molecular chemosensors baesd on pincer platinum group metal complexes .....	6
1.2.2 Optical molecular chemosensors baesd on cyclometalated platinum group metal complexes .....	10
<b>1.3 The objective of the dissertation</b> .....	16
References .....	16
<b>Chapter 2 A tetranuclear cyclometalated palladium-azo complex MOP as an optical molecular chemosensor for the detection of organophosphorus pesticides (OPPs)</b> .....	24



<b>2.1 Introduction</b>	24
<b>2.2 Synthesis and characterization of the molecular probe</b>	26
2.2.1 Preparation of MOP	27
2.2.2 Characterization of MOP	27
<b>2.3 Results and discussion</b>	29
2.3.1 Chromogenic reaction of MOP with OPPs	29
2.3.2 Investigation on the reaction mechanism of MOP with OPPs	31
2.3.3 Effect of solvent on the chromogenic reaction of MOP with OPPs	31
2.3.4 Investigation of the feasibility using MOP for quantitative analysis of OPPs	32
Summary	35
Reference	36

### **Chapter 3 A dinuclear cyclometalated palladium-azo complex mop as an optical molecular chemosensor for the determination of thiocyanate anion in aqueous solution**

<b>3.1 Introduction</b>	39
<b>3.2 Synthesis of the molecular probe</b>	40
<b>3.3 Results and discussion</b>	41
3.3.1 Differential spectral recognition of mop to thiocyanate	41
3.3.2 Investigation on the reaction mechanism of mop with thiocyanate	42
3.3.3 Optimization of the experimental conditions for the sensing reaction	44
3.3.4 Analytical performance of the method for the quantitative analysis of thiocyanate	45

Summary .....	47
References .....	48

## **Chapter 4 Preliminary investigation on the application of MOP**

### **to detections of bioactive targets .....51**

#### **4.1 Investigation on the application of MOP in the recognition of phenol and aniline compounds.....51**

##### **4.1.1 Introduction .....51**

##### **4.1.2 Results and discussion .....52**

###### 4.1.2.1 Chromogenic reaction of MOP with phenol and aniline compounds .....52

###### 4.1.2.2 Investigation on the reaction mechanism of MOP with phenol and aniline compounds .....52

#### **4.2 Investigation on the application of MOP in the recognition of penicillin G and its metabolism products .....54**

##### **4.2.1 Introduction .....55**

##### **4.2.2 Results and discussion .....55**

###### 4.2.2.1 Chromogenic reaction of MOP with ampicillin.....56

###### 4.2.2.2 Differential spectral recognition of MOP to penicillin G .....56

###### 4.2.2.3 Investigation on the reaction mechanism of MOP with penicillin.....56

##### Summary .....57

##### References.....59

## **Chapter 5 Conclusion and prospect of this dissertation .....62**

### Appendix 1 Apparatus and reagents used in this dissertation .....64

Appendix 2 Publications and presentations during author's studying for Master's degree.....	65
Acknowledgements .....	66

厦门大学博硕士论文摘要库

# 环金属化钯-偶氮配合物作为光学分子传感器的 应用初探

## 摘要

光学分子传感器是“分子识别”研究在分析科学新的发展需求下的一种应用形式。由于其在环境或生物微观系统的组成、结构和衍化信息探索等方面的重要作用而日益得到重视。本论文成功地应用了一类环金属化钯-偶氮配合物作为光学分子传感器，其传感的目标物种涉及阴离子、中性有机小分子（如有机磷农药）等几类物种。论文分五章，分别包括以下主要内容：

### 第一章 绪论

首先简要介绍了光学分子传感器的基本概念和基本设计思路，接下来重点综述了铂族金属配合物作为光学分子传感器的研究进展，最后对这些相关研究进行分析和总结，结合本实验室的工作基础，提出本论文的研究设想。

### 第二章 四核环金属化钯-偶氮配合物 MOP 作为有机磷农药检测的分辨型光学分子传感器

本章利用环金属化配合物(cyclometalated complexes)的化学特性，结合我们研究组曾开发出的一类新型的分辨型光学分子传感器 MOP，考察了其对有机磷农药的选择性光谱响应能力和对不同含硫代磷酸酯骨架的有机磷农药组分的光谱分辨能力。实验表明：在 DMF—acetone 的混合溶剂中，MOP 对含硫代磷酸酯的有机磷农药有高的选择性识别能力，而对氧磷类有机磷农药（如敌敌畏）则没有光谱响应，而且 MOP 对具有不同磷酸酯骨架的硫磷类农药有较强的光谱分辨能力，籍以建立相关组分的光谱检测新方法。

### 第三章 双核环金属化钯-偶氮配合物 mop 作为水溶液中硫氰酸根测定的光学分子传感器

本章利用钯-偶氮配合物 Pd-Cl-Pd 桥键的反应性能, 结合铂族金属化合物对外来配体所具有的独特的分辨性光谱响应的特点, 设计了水溶液中硫氰酸根的一种新型的光学分子传感器 mop。实验表明: 1) 在水溶液中, mop 对硫氰酸根体现出优异的识别专一性, 对其它无机阴离子几乎没有响应; 2) 传感过程可以在较宽的 pH 范围 (5.8-8.0) 和高浓度的常见阴离子共存下进行, 具有良好的可操作性和实用性; 3) 以 mop 为探针, 可以在生理 pH 的水溶液中实现对硫氰酸根在  $10^{-7}$  mol/L 水平上的定量测定。这是一种全新的硫氰酸根的光学传感理念, 由于硫氰酸根阴离子在生理学和医学方面的重要性, 这种光学分子传感器可望在相关的研究领域中得到借鉴和应用。

### 第四章 MOP 在其它生理活性物种检测方面应用的初探

本章阐述了环金属化钯-偶氮配合物在有机小分子的分辨性传感方面的应用。实验研究了 MOP 对苯胺、苯酚类化合物以及青霉素 G 的代谢产物的识别, 同时探讨了其传感机理, 为拓展 MOP 分子探针的在分析化学中的应用作了初步探索。

### 第五章 论文的总结与展望

**关键词:** 光学分子传感器, 环金属化钯-偶氮配合物, 有机磷农药, 硫氰酸根

# **Investigation on the application of cyclometalated palladium-azo complexes as optical molecular chemosensors**

## **Abstract**

Optical molecular chemosensor (OMCS) has increasingly been important due to its distinct characteristic in probing the composition, structure and evolution of environmental or biological microsystems, and what's more, optical molecular chemosensor (OMCS) has an explosive growth in analytical chemistry. Some OMCSs have been developed in this dissertation based on a cyclometalated palladium-azo complex, where a wide range of chemical substances, including some important anions and neutral organic small molecules such as organophosphorus pesticides, were explored as the sensing targets. This dissertation consists of five chapters summarized as follows.

In chapter 1, a general introduction to OMCS was presented. Emphasis was paid on the new developments of OMCS, especially those based on platinum group metal complexes. Based on reviewing the research progresses of using cyclometalated palladium-azo complexes as optical molecular chemosensors, the objective of this dissertation was presented.

In chapter 2, a tetranuclear cyclometalated palladium-azo complex (MOP) was synthesized according to our previous work and applied as a differential colorimetric molecular chemosensor for organophosphorus pesticides (OPPs) for the first time. This molecular probe was found to have highly selective

recognition ability to OPPs. In a DMF-acetone mixed solvent, it showed no spectral response to oxophosphate pesticides, but exhibited differential absorption spectra in the presence of different sulfur phosphorus pesticides (SPPs), which could be used for the determination of SPPs.

In chapter 3, a dinuclear cyclometalated palladium-azo complex mop was synthesized and used as an optical molecular chemosensor for thiocyanate in aqueous solution. The developed probe has the following characteristics: 1) It was found to sensitively show obvious color change upon addition of  $\text{SCN}^-$  into an aqueous solution of the probe at pH 7.0, while never show color changes upon addition of  $\text{F}^-$ ,  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$ ,  $\text{HCO}_3^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{CH}_3\text{COO}^-$ , et al.; 2) The absorption spectra induced by the target species hardly changed in the pH range from 5.8 to 8.0, which provides a great convenience for the feasible application; 3) The sensing of  $\text{SCN}^-$  could be performed in the presence of coexisting common anions at high concentrations; 4)  $\text{SCN}^-$  at the concentration level of  $10^{-7}$  mol/L could be well quantitatively titrated by mop at pH 7.0. Since  $\text{SCN}^-$  is of great importance in biological chemistry, the developed probe was expected to see its application in the related research fields.

In chapter 4, MOP was further applied to sensing other bioactive targets such as phenol- or aniline-based compounds and the metabolic products of penicillin G. The sensing mechanism was also proposed. Thus attempts were made to extend the application of MOP probe in analytical chemistry.

At last, the main features and innovations of this dissertation were described.

**Keywords:** optical molecular chemosensors, cyclometalated

**palladium-azo complexes, organophosphorus pesticides,  
thiocyanate**

厦门大学博硕士论文摘要库



Degree papers are in the "[Xiamen University Electronic Theses and Dissertations Database](#)". Full texts are available in the following ways:

1. If your library is a CALIS member libraries, please log on <http://etd.calis.edu.cn/> and submit requests online, or consult the interlibrary loan department in your library.
2. For users of non-CALIS member libraries, please mail to [etd@xmu.edu.cn](mailto:etd@xmu.edu.cn) for delivery details.

厦门大学博硕士论文摘要库